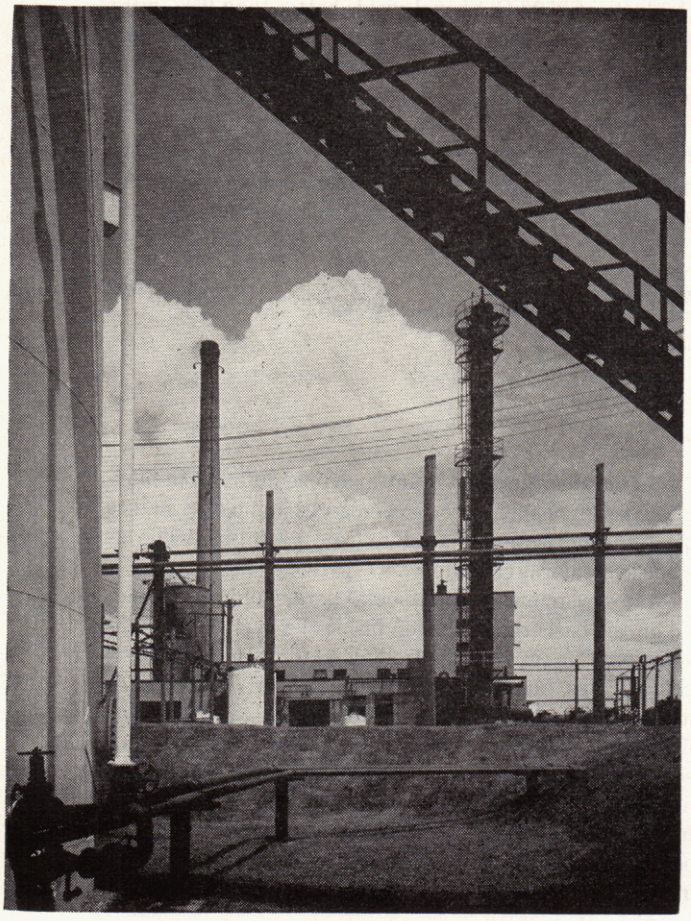


FORMALDEHYDE FROM METHANOL

RODNEY N. HADER

Associate Editor

in collaboration with

R. D. WALLACE AND R. W. McKINNEY

Spencer Chemical Co., Calumet City, Ill.

Raw Methanol Storage Tank (*Extreme Left*) and Stripping Column (*Center*) Which Removes Methanol from Final Product

A Staff-Industry Collaborative Report

NEARLY a hundred years ago, the chemist Butlerov (*6*), working with derivatives of methylene iodide, allowed the iodide to react with silver acetate and then hydrolyzed the resulting solution. A vapor with an irritating and pungent odor was evolved, but because of a mistake in the determination of vapor density, Butlerov failed to identify it as formaldehyde. A few years later, however, in 1867, the German professor, Hofmann (*9, 10*), prepared formaldehyde and recognized it as such. Hofmann's method consisted of passing methanol and air over a heated platinum spiral—a process closely analogous to that now widely used in commercial formaldehyde production.

It was not until 1892 that Kekulé isolated the first monomeric formaldehyde of relative purity and some years thereafter that the chemical attained industrial significance. The earlier work of Loew (*12*) and Tollens (*20*), which indicated that Hofmann's process could be conducted feasibly on a continuous basis, played a very important role in pushing formaldehyde toward commercial production.

Simplest and least characteristic of the aliphatic aldehydes, formaldehyde today is greatest in technical importance of all the aldehydes that figure in modern chemical industry. Because of its versatility (it reacts with nearly all compounds, both organic and inorganic), formaldehyde has continued to find new uses year after year, and production has mounted logarithmically since the period of the first world war. This is shown in Figure 1.

By a comfortable margin, the greatest outlet for formaldehyde production is the resins and plastics field, which utilizes large amounts in phenolic, urea, and melamine resins (Figure 2). As early as 1935, resins and plastics were accounting for more than 50% of total formaldehyde consumption, and except for the war years 1943–45, they have continued to do so. During World War II, large quantities of formaldehyde were used in the manufacture of hexamethylenetetramine (hexamine) for RDX explosive. In the years 1943–45, this use alone averaged nearly 100,000,000 pounds per year or about 20% of total consumption, thus accounting for the relatively poorer showing of plastics on a percentage basis. The production of hexamine specifically for RDX is considered a special use of formaldehyde, and the quantities so consumed have not been included in Figure 2 under formaldehyde consumption for hexamine production.

In 1951, about 64% of formaldehyde production entered resins and plastics. Industrial chemical uses, such as the production of hexamine, pentaerythritol, ethylene glycol, and rubber chemicals, accounted for about 34%. The small remainder went into textile dyes and intermediates, leather chemicals, embalming fluid, drugs and pharmaceuticals, paper, adhesives and protective coatings, disinfectants, insecticides, and photography.

The most common commercial solution of formaldehyde shipped in the United States is an aqueous solution of 37% formaldehyde with 1 to 7% methanol added as an inhibitor or stabilizer. The methanol prevents precipitation of polymers that form in the solution on long standing, particularly at moderate or low temperatures. Pure gaseous formaldehyde polymerizes slowly at ordinary temperatures; the polymerization is catalyzed by small quantities of water vapor, formic acid, acetic acid, and other polar impurities. Formic acid is the impurity most frequently

responsible for inducing polymerization in commercial solutions. The polymerization is illustrated by the following equations:

$$HC(=O)-H + HC(=O)-OH \rightarrow HC(=O)-OCH_2OH \quad (1)$$

$$HC(=O)-OCH_2OH + nHC(=O)-H \longrightarrow HC(=O)-O(CH_2O)_nCH_2OH \quad (2)$$

Liquid formaldehyde polymerizes rapidly at the low temperature of −80° C., unless extremely pure. Even methanol, normally an inhibitor, will give a violent reaction when added to the liquid at that temperature, resulting in solidification of the mixture. On warming to room temperature, the solid reverts to a clear liquid. Maintaining formaldehyde solution at somewhat elevated temperature is one common means of preventing polymer precipitation.

On long storage, commercial grades of aqueous formaldehyde gradually become acidic, and the aldehyde strength declines. The following reactions are believed to be responsible (*21*):

$$HC(=O)-H + 2CH_3OH \longrightarrow CH_2(OCH_3)_2 + H_2O \quad (3)$$

$$2HC(=O)-H + H_2O \longrightarrow CH_3OH + HC(=O)-OH \quad (4)$$

$$2HC(=O)-H + O_2 \longrightarrow 2HC(=O)-OH \quad (5)$$

Reaction 3 occurs under acidic conditions and is catalyzed by impurities such as iron, zinc, or aluminum. Reaction 4 will occur under acidic conditions but proceeds most rapidly under alkaline conditions. Reaction 5 occurs through exposure to air.

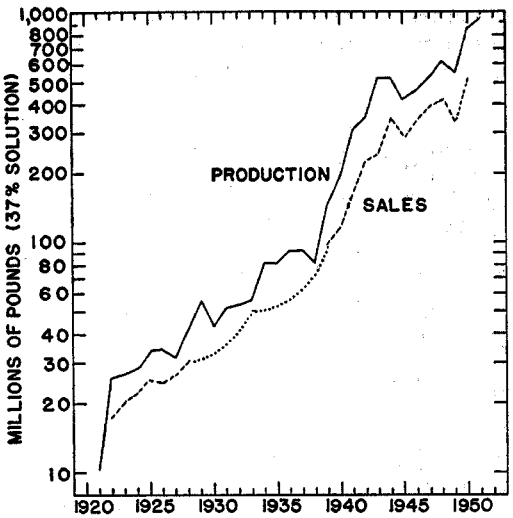


Figure 1. U. S. Production and Sales of Formaldehyde

(Adapted from *Chemical Economics Handbook*, Stanford Research Institute, based on U. S. Tariff Commission Data)

Besides the aqueous solutions, which constitute the bulk of formaldehyde production, solid forms of the material also are available in commercial quantities. The most important of these is paraformaldehyde, a solid polymer of varying molecular weight, containing up to about 5% water. Industrial use of this material has been limited by its higher cost as well as by the excessive reactivity of the monomer secured from it on depolymerization; maintaining control over reactions involving this monomer is generally more difficult than is the case with ordinary formalin solutions.

Paraformaldehyde, or commercial "trioxymethylene," is sometimes erroneously called trioxane. The latter, however, is a unique solid, trimeric form of the aldehyde and is actually a true cyclic ether. It is a relatively stable compound, but it can be decomposed by strong acids to yield monomeric formaldehyde in perhaps its most reactive form. The trimer is of interest principally in special preparations where exact amounts of anhydrous formaldehyde are desirable (*22*).

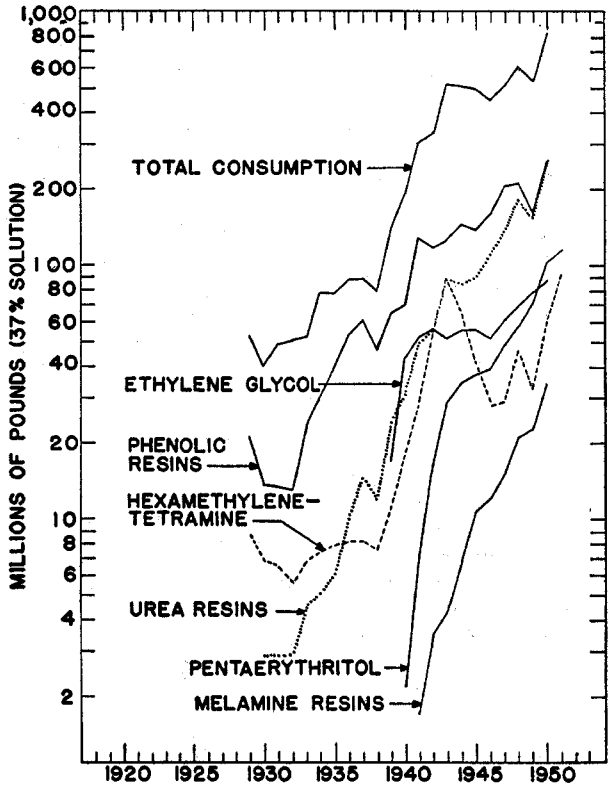


Figure 2. U. S. Formaldehyde Consumption Pattern

(Adapted from *Chemical Economics Handbook*, Stanford Research Institute, based on U. S. Tariff Commission Data)

In his A.C.S. Monograph, Walker (*21*) presents detailed discussions covering the properties, reactions, analysis, and uses of formaldehyde and its commercial solutions.

MANUFACTURING PROCESSES

The oldest commercial method of preparing formaldehyde is still in use, essentially unchanged except for refinements. Consisting of the oxidation and dehydrogenation of methanol with air over a metallic gauze catalyst, it is an easy method with few by-product complications.

Commercial Processes Using Methanol

Commercial production in the United States was initiated in 1901 by the Heyden Chemical Works of America, now Heyden Chemical Corp. The process was a modification of a German process, using a copper catalyst; output was quite small (*13*). The replacement of copper by silver gauze as catalyst came early, and most tonnage producers today use silver in some form. Formaldehyde yields with silver gauze are generally 85 to 90%, based on the methanol consumed. Higher yields have been claimed for systems using special forms of silver, notably electrolytic silver crystals (*3–5*).

In the production of formaldehyde from methanol, the principal reactions are:

$$CH_3OH + O_2 \longrightarrow HC(=O)-H + H_2O + 36{,}800 \text{ g. cal./g. mole} \quad (6)$$

$$CH_3OH \longrightarrow HC(=O)-H + H_2 - 28{,}800 \text{ g. cal./g. mole} \quad (7)$$

The importance of Reaction 7 was not fully appreciated by early formaldehyde manufacturers, who incorrectly assumed that the conversion of methanol to formaldehyde was entirely one of direct oxidation. It had been shown as early as 1920, however, that the methanol-to-air ratio had a strong influence in determining conversions and net yields. Thomas (*19*) showed that increases in this ratio increased net yield but decreased manufacturing conversion; Thomas recommended reaction mixtures of 30 to 41% methanol by volume.

Most of the important progress in boosting conversion during the 1930's was due to the increased exploitation of the endothermic dehydrogenation reaction. Through careful selection of catalyst and through finer control of operating conditions, it was found possible to encourage Reaction 7 and maintain an optimum balance between the two principal reactions in the converter. The methanol content of converter effluent was thus gradually reduced from more than 55% to less than 15% in commercial plants (*11*).

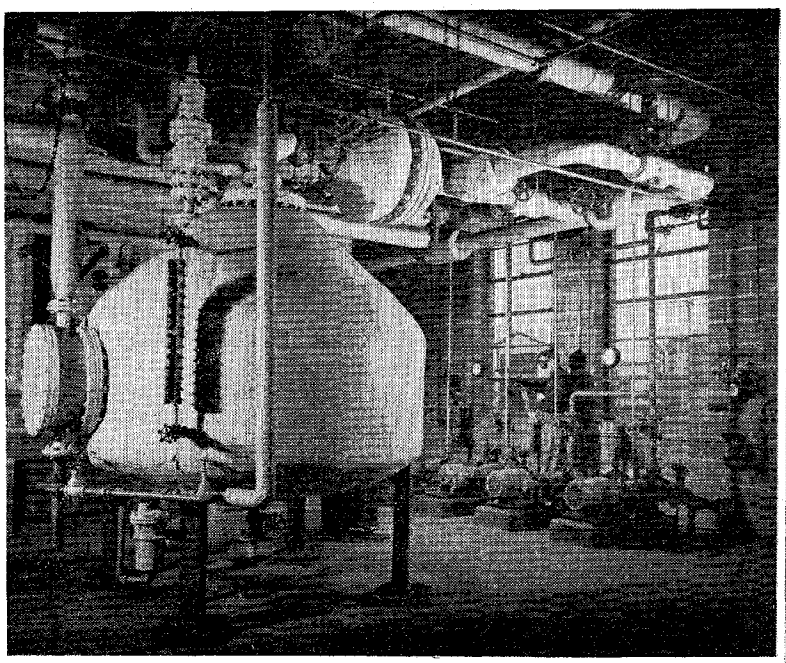
The mode of producing formaldehyde commercially from methanol differs but little from company to company where the silver gauze process is used (*15*, *16*). An entirely different oxidation process is known, however, and is used by Du Pont for at least part of its formaldehyde production. In this alternative process, the reaction is true oxidation with no dehydrogenation; the reaction is catalyzed by iron-promoted molybdenum oxide and is capable of conversions and formaldehyde yields well above 90% (*1*). Furthermore, because of the high conversion the product contains little or no methanol, and the need for distillation to produce a salable product is eliminated. This oxidation process operates at temperatures from 350° to 450° C., instead of the 600° C. which is normal with a silver catalyst. In its manufacture of ethylene glycol, the Du Pont Co. uses formaldehyde which has been produced by this alternative method; the company uses silver gauze and special forms of silver in some of its other production units.

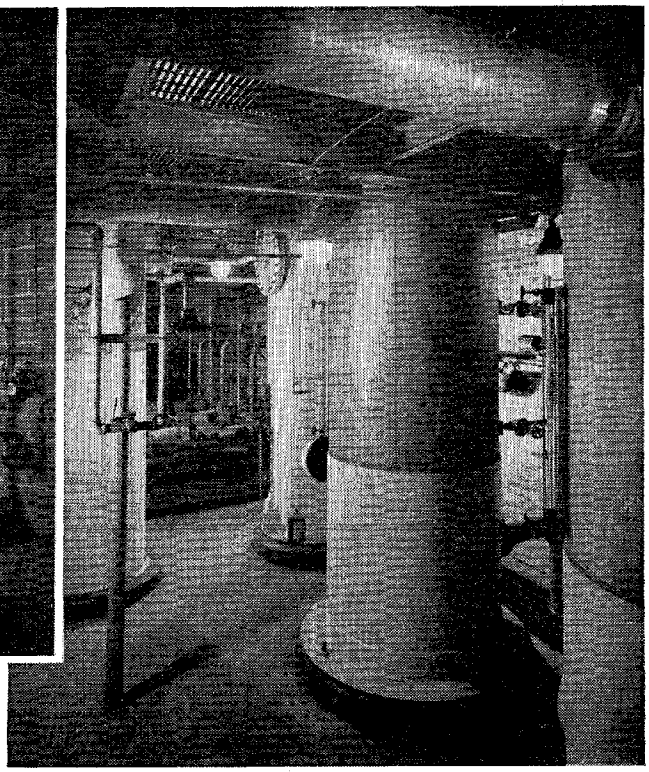
An interesting multistage variation of the formaldehyde-from-methanol process has recently come to light (*7*); it is related to the Du Pont oxidation process, particularly with regard to catalyst, but as yet it has not been incorporated into any production unit. In the multistage process, a stream of air flows through several successive catalyst beds, with methanol vapor injected into the air stream between beds. As the air stream and reaction products progress through the reactor, methanol is added in steps, until, by the time the last stage is reached, the stoichiometric amount has been introduced. This process, thus far carried through the pilot plant stage, has been found to be an efficient method for obtaining high yields, with the added advantage of a reactor effluent containing formaldehyde in unusually high concentrations.

Since the absorption or scrubbing step in commercial formaldehyde production is generally the capacity-limiting factor, a highly concentrated effluent of this kind is most desirable, providing for greater capacity with equipment of a given size. In experimental runs, the multistage process has been found to achieve 91 to 93% conversion of methanol to formaldehyde, yielding an exit gas containing 1% oxygen, about 0.1% methanol, less than 1% carbon monoxide, and more than 16% formaldehyde. The catalysts found successful in this process were iron-promoted molybdenum oxide and molybdenum-promoted manganese phosphate. Silver catalysts failed to give satisfactory performance in the experimental apparatus.

Other Processes

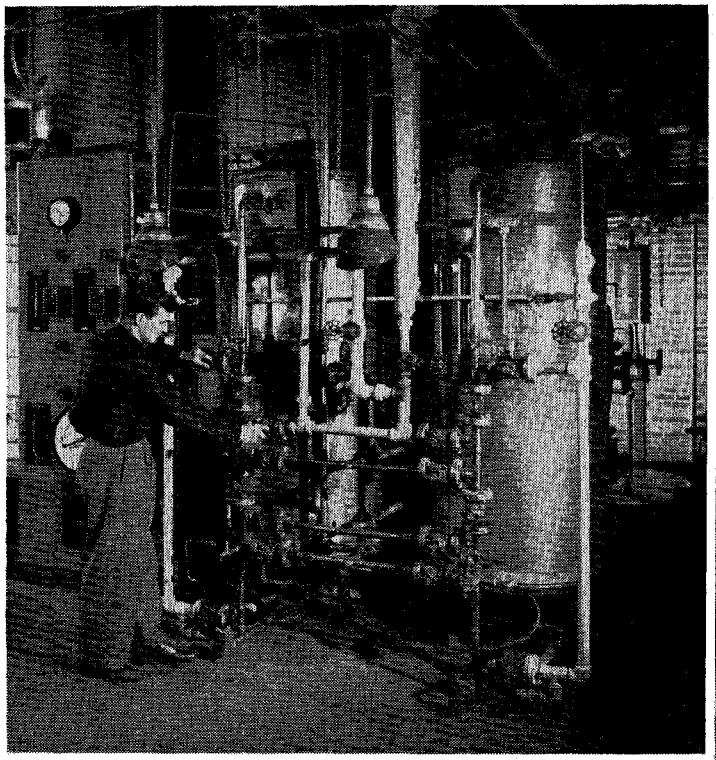
Far behind the methanol process tonnagewise is one that uses natural gas as raw material. A plant based on this process has



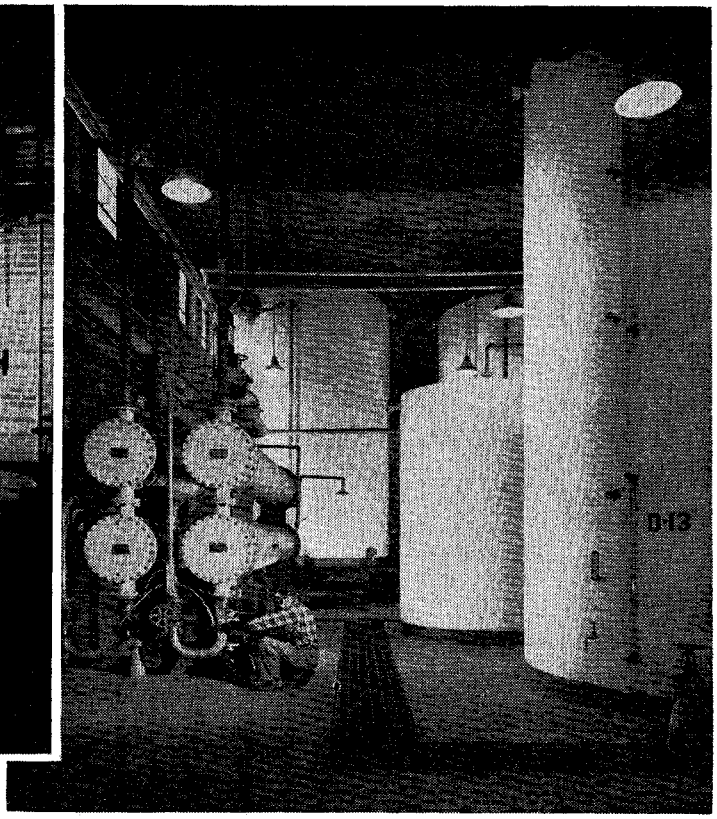


(*Left*) **Methanol Evaporator with Vapor Superheater Above It.**

(*Right*) **Absorber Room Showing Primary Absorbers and Final Absorber and Caustic Air Scrubber**



Ion Exchange Unit Removes Traces of Formic Acid from Formaldehyde



Tank Storage Room Showing Product Weigh Tank (*Left Rear*) and Absorber Stream Coolers (*Left Foreground*)

been operated commercially since 1928 by Cities Service Oil Co. at Tallant, Okla. Substantial effort has been expended both in the United States and in Europe to make this process a major source of formaldehyde, but poor yields, complications from side reactions and from product purification requirements, and high initial investment have combined to hold the process in a relatively low second place. Methanol is produced as a coproduct in amounts approximately equal to the tonnage of formaldehyde produced. Other by-products, such as acetaldehyde and ketones, are produced in smaller amounts. The main reactions for the process are

$$CH_4 + O_2 \longrightarrow HC(=O)-H + H_2O \quad (8)$$

$$2CH_4 + O_2 \longrightarrow 2CH_3OH \quad (9)$$

The side reactions, which cut the yield, involve the formation of combustion products, principally the oxides of carbon.

Similar to the natural gas process is that used by Celanese Chemical Corp., with propane or butane as its hydrocarbon source (*13*, *21*).

Very little hope is held for the possibility of synthesizing formaldehyde from carbon monoxide and hydrogen, since only trace quantities of the aldehyde are produced when carbon monoxide and hydrogen are passed over a catalyst at atmospheric or slightly elevated pressures. Furthermore, any catalyst that promotes the formation of formaldehyde in this system will also catalyze its further hydrogenation to methanol (*14*). There are no formaldehyde plants operating in the United States with this reaction as a basis, although several patents have been issued in this field (*8*, *17*, *18*, *23*).

The decomposition of methylal in the presence of acids yields formaldehyde and methanol in the following manner:

$$CH_2(OCH_3)_2 + H_2O \longrightarrow HC(=O)-H + 2CH_3OH \quad (10)$$

Celanese Chemical Corp. in 1947 announced the availability of methylal in large scale quantities, but the compound is not expected to become a primary source of formaldehyde. Its chief use is as a solvent chemical.

Laboratory experiments have shown that under certain conditions ethylene is oxidized to formaldehyde in yields of 50% (*2*). The reaction is believed to proceed as follows:

$$CH_2{=}CH_2 + {}^1/_2O_2 \longrightarrow CH_2{=}CHOH \quad (11)$$

$$CH_2{=}CHOH \longrightarrow CH_3C(=O)-H \quad (12)$$

$$CH_3C(=O)-H + {}^1/_2O_2 \longrightarrow CH_2OHC(=O)-H \quad (13)$$

$$CH_2OHC(=O)-H \longrightarrow 2HC(=O)-H \quad (14)$$

Catalysts, concentrated gases, high temperatures, or prolonged heating may cause the oxidation to proceed to completion, with the formation of carbon dioxide.

SPENCER CHEMICAL CO. PLANT AT CALUMET CITY, ILL.

When, in 1947, the Spencer Chemical Co. first considered the possibilities of entering the formaldehyde field as a producer, demand considerably exceeded the supply available from the 17 commercial plants then operating. Price trends, because of the supply-demand imbalance, tended to be upward.

After a survey of potential markets, shipping facilities, and existing formaldehyde plants, Spencer chose its site in the Chicago area. By January 1949, barely one year after the final decision

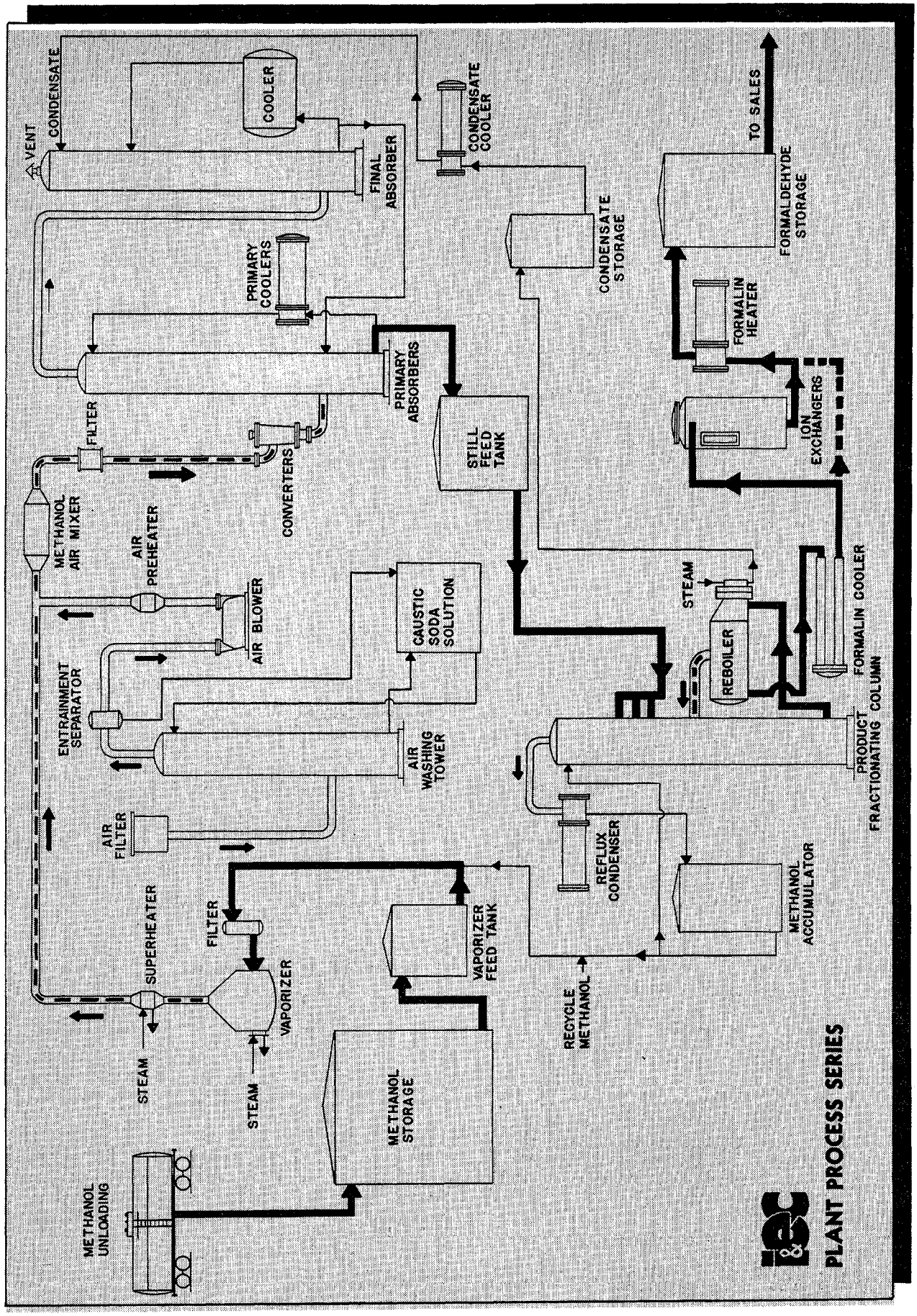


Figure 3. Flow Sheet for Production of Formaldehyde from Methanol at Calumet City, Ill., Plant of Spencer Chemical Co.

to proceed, the new plant was producing its rated 50 tons per day of 37% formaldehyde solution. First substantial formaldehyde plant in the Chicago area, Spencer's installation is in a commanding position geographically. The nearest formaldehyde plant is at Toledo, Ohio, more than 200 miles away.

Shipping economics dictated location of the formaldehyde plant in a consuming area rather than at the company's main plant site at Pittsburg, Kan. Spencer produces its own methanol at Pittsburg, but it is considerably more economical to ship methanol for conversion to formaldehyde in the Chicago area than it would be to ship Pittsburg-produced formaldehyde solution. Two factors are involved: Since the standard 37% formaldehyde solution is more than 50% water by weight, a large share of shipping costs would be required for the transporting of water. In addition, railroads make a distinction in freight rates between raw materials and finished products. By shipping methanol at the lower raw materials freight rate, instead of finished formaldehyde solution at the higher end products rate, a significant saving can be realized.

Personnel

Since the Spencer Chicago Works plant is fully instrumented for virtually automatic operation, a small operating staff is able to maintain production at rated capacity with a minimum of fluctuation. The entire staff numbers 17, including office personnel. An administrator and a supervisor, both technically trained, are assisted by an engineer in scheduling and planning and in directing the activities of the production crew. Two regular maintenance men on the day shift keep equipment in proper working order. Ten operators, three on the day shift, two each on the twilight and night shifts, and a relief operator for each shift are able to handle the entire production operation.

Methanol

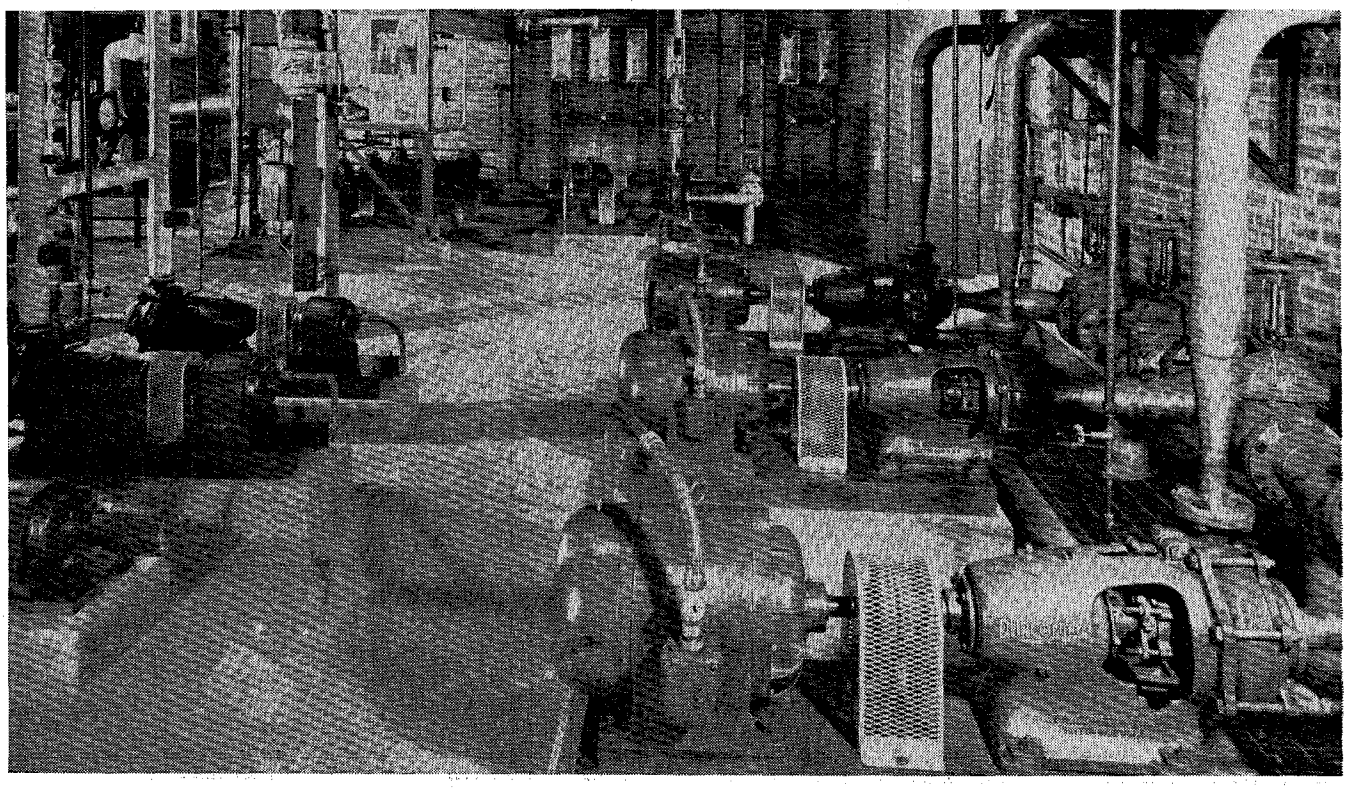
Figure 3 is a flow sheet for Spencer's formaldehyde process. Methanol for the reaction is shipped in 8000- or 10,000-gallon tank cars from Spencer's Pittsburg plant. At the Chicago Works it is transferred by centrifugal pump into either of two 88,000-gallon carbon steel outdoor storage tanks or directly into the methanol scale tank within the plant. All methanol is weighed into the process to permit an accurate material balance.

With a capacity of 8250 gallons, the scale tank will supply methanol for $26^1/_2$ hours of continuous plant operation at full production rate. A small alternate feed tank with a capacity of 1270 gallons is used to supply methanol for the process while the scale tank is being filled. The small tank holds enough methanol for 4 hours of operation, providing a comfortable margin of safety; the scale tank can be filled in 25 to 30 minutes.

From the scale tank, methanol is pumped into the evaporator (*24E*). A valve actuated by a liquid level controller on the evaporator maintains the rate of methanol feed. All recycled methanol from the process is returned to the evaporator; the liquid level controller adjusts only the flow of make-up from fresh methanol stock.

In the evaporator, a steam coil supplied with steam at 30 pounds per square inch gage supplies heat for the vaporization of the alcohol. The evaporator is of the horizontal tube, kettle type; it is 6 feet in diameter and $7^1/_2$ feet in over-all height. A pressure-controlled valve on the steam line controls steam flow to maintain a methanol vapor pressure in the evaporator between 25 and 40 pounds per square inch.

From the evaporator, the methanol vapor passes through a superheater, where steam at a pressure of 150 pounds per square inch raises the temperature of the methanol vapor to about 108° C. The 12 copper tubes in the superheater are finned (*26E*); vapor flow is parallel to the fins. The vapor from the superheater passes through a pressure control valve which adjusts downstream pressure to a constant level for flow measurement purposes. A control valve, which is operated manually from the main panel board, is used to adjust the flow of methanol vapor into the methanol-air mixer; the latter supplies feed to the converters.



Pumps Are Grouped for Easy Maintenance

Air Supply

Oxygen for the conversion of methanol to formaldehyde is supplied by air. Outdoor air is drawn into the plant through a wool-felt filter and passed into a washing tower which has a 30-inch by 10-foot section packed with 2 × 2 inch ceramic rings. There the air is washed with 5% sodium hydroxide solution flowing downward over the packing at 2 to 3 gallons per minute. This operation removes sulfur dioxide, carbon dioxide, and minute particles of foreign matter, any of which might have a seriously deleterious effect on the catalyst. Through evaporation of water into the air stream, the caustic solution gradually builds up in concentration. Every week it is rediluted to 5%, when the solution becomes too dirty for further use, it is diluted to very low concentration, discarded, and replaced by fresh 5% solution.

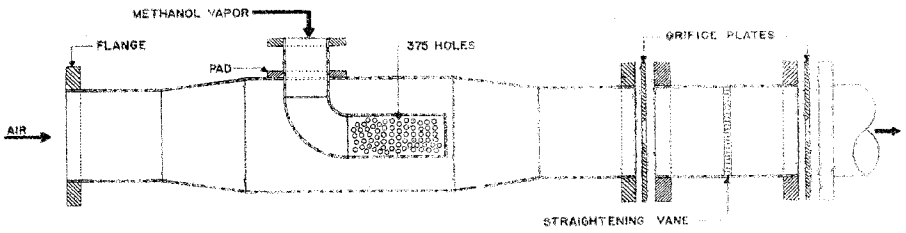


Figure 4. Methanol-Air Mixer

From the washer, the air passes through an entrainment separator and into the suction side of a centrifugal blower. Two blowers (*10E*) are connected in parallel; one is held ready for substitution in the event that the operating blower requires maintenance. The blowers are driven by steam turbines (*2E*) operating on steam at 150 pounds per square inch. Connected directly by special high speed couplings, the turbines drive the blowers at 3500 r.p.m.

From the blower, the air passes through a preheater where steam at 30 pounds per square inch heats it to about 54° C. The preheater contains 12 finned tubes (*26E*) in two rows; air flow is parallel to the fins.

The hot air leaves through a pressure controlling valve which maintains a constant downstream pressure for flow measurement purposes. An automatic ratio flow controlling valve meters the heated air into the methanol-air mixer (*1E*). A diagram of the mixer is shown in Figure 4.

Reaction

The methanol-air mixture, which leaves the mixer at about 77° C., is filtered as a double check on purity of the gas stream, since even very small amounts of extraneous materials will poison the reaction catalyst. For example, as little as 0.1 gram of iron deposited on a converter's catalyst charge will promote the carbonization of methanol and kill catalyst activity completely in as little as 12 hours. The filter is a stainless steel unit with glass fiber inserts.

From the filter, the gas mixture passes through a flame arrester and thence into a manifold which supplies the converters. These are connected to the inlet manifold by expansion connectors; 100 converters are connected in parallel in four banks. One flame arrester is supplied on the inlet side of each bank of 25 converters; on the outlet side, converter banks are paired, and one flame arrester is supplied for each pair.

Converter size is optional; Spencer chose to employ a large number of small-size converters in order that only a very small fraction of production would be lost in the event of breakdown in any given converter. The use of a great number of small vessels, however, tends to increase the total amount of maintenance attention required. It could be particularly serious if a contaminated feed stream were permitted to enter the manifold, poisoning the catalyst in all converters simultaneously.

Catalyst

Silver, placed on catalyst supports in the converters, is used to catalyze the conversion of methanol to formaldehyde; the gas mixture flows downward through the interstices in the catalyst. Only a very slight pressure drop—0.1 to 0.2 inch of mercury—is caused by the catalyst's resistance to flow.

The gas mixture is given only one pass through the catalyst, and conversion of about 60% is realized. This is equivalent to catalyst efficiency of over 90%. Slight losses through side reactions, consisting primarily of carbon monoxide and carbon dioxide formation, account for another 3 to 5% of the methanol feed, and the remainder passes through the converters unchanged. It has been found that virtually all the conversion accomplished occurs at or very near the upper edge of the silver catalyst. The principal function of the additional catalyst is to dissipate the large amounts of heat released. The temperature drop between the upper edge of the catalyst and a thermocouple placed below the catalyst support is about 150° to 200° C. The actual reaction temperature is normally about 600° C.

Absorption

Exit gases from the converters flow through flame arresters and into two primary absorbers ($37^3/_4$ feet in height by $3^1/_2$ feet in diameter), which are packed 20 feet high, with 2 × 2 inch Raschig rings (about 162 rings per cubic foot) providing a surface area of 28 square feet per cubic foot of column space. Each primary absorber handles the flow from two banks of converters.

In the primary absorbers, a circulating methanol-formaldehyde-water solution removes the major portion of condensable vapors from the gas stream. The gases enter the bottom of the absorber column at the rate of about 3200 pounds per hour and flow upward countercurrent to the descending spray of methanol-formaldehyde-water solution. The solution flows at the rate of about 250 gallons per minute; from the column base it is pumped through a cooler and recirculated to the top of the absorber.

The vapors not condensed or absorbed in the primary absorber leave the top, pass through an entrainment separator, and flow into the bottom of the final absorber. The final absorber is 51 feet, 2 inches in over-all height and 28 inches in diameter. It contains a total of 16 cascade-type trays (*9E*), divided into two sections. In the lower four trays, a dilute aqueous solution of methanol and formaldehyde is recirculated and sprayed downward to absorb most of the organic vapors in the stream from the primaries. In the upper section, pure steam condensate is added to ensure virtually complete removal of all organic material before the waste gas stream is exhausted to the atmosphere. Condensate must be used because specifications for the final product are so rigid that the plant's normal supply of city water is not sufficiently pure. Figure 5 indicates the design of the cascade-type trays used in the final absorber and in the methanol stripping column further along in the process.

The solution that recirculates in the lower portion of the final absorber is passed through a cooler and then back into the tower. At times, particularly in the summer months when the cooling water (river) temperature is not low enough to hold the recycle solution temperature below 24° C., the recirculating stream is passed through an ammonia refrigerating system for additional cooling. The fresh condensate used as make-up in the upper section of the final absorber is refrigerated in this manner, also.

A single final absorber with a recirculation rate of about 10 gallons per minute and a condensate make-up rate of about 3 gallons per minute handles the exit vapors from both primaries. As the concentration of formaldehyde and methanol builds up in the final absorber solution, a portion of the liquid stream is diverted for use as make-up in the primary absorbers. As the concentration builds to a high level in the primary absorbers, a liquid level controller releases a portion of the strong solution, which is then pumped to the still feed tank. The formaldehyde content of the primary absorber solution must be maintained above the minimum desired in the final product. Ultimate control over this concentration in the primary is maintained by controlling the rate of condensate addition in the final absorber.

Distillation

The strong solution from the bottom of the primary absorbers is accumulated in the 3010-gallon still feed tank. This solution is pumped through a flow control valve into the stripping section of the distillation column. The column contains 35 cascade-type trays (*9E*). Multiple connections allow the use of the 16th, 18th, or 20th tray (from the top) as feed tray; tray No. 18 is normally used. Bottoms from the stripping column flow through a 5-inch line to the reboiler (*25E*), a shell-and-tube heat exchanger supplied with steam at 30 pounds per square inch. Methanol-water vapor leaving the reboiler is returned through a 14-inch line to the stripping column base.

Temperature control on the column is maintained through a thermocouple on tray No. 26. The temperature on this tray is held constant through automatic control of the flow of steam to the reboiler. The head temperature of the column is maintained at about 64° C., or approximately the boiling point of methanol. It is controlled by regulating the flow of reflux to the column.

Methanol vapor leaving the column passes into a condenser, and the condensate is accumulated for return to the tower as reflux. A level controller on the accumulator tank automatically returns excess methanol to the evaporator which feeds the converters early in the process.

The formaldehyde solution withdrawn from the bottom of the distilling column reboiler is cooled by passage through a shell-and-tube heat exchanger (*8E*) with finned tubes. The product flows inside the inner tubes with cooling water in the annular space outside; fins are on the water side. Product pumps transfer the cooled solution to small run-down tanks and thence either into a weigh tank or directly into the ion exchange units.

Normal sequence is for the product to accumulate temporarily in the run-down tanks before ion exchange treatment and final weighing prior to shipment. The ion exchange step is normally handled on the night shift, so that each morning the entire production from the previous day has been purified and collected in the scale tank ready for shipment.

Table I. Product Specifications for Commercial Aqueous Formaldehyde Solutions

	Nominal Weight Ratio, Formaldehyde: Methanol		
	37:1	37:7	45:1
Formaldehyde, % by wt.	37.0 min. 37.3 max.	37.0 min. 37.3 max.	44.9 min. 45.5 max.
Methanol, % by wt.	.... 1.0 max.	6.5 min. 7.5 max.	.... 1.4 max.
Acidity (as formic acid), %	0.04 max.	0.03 max.	0.03 max.
Iron, p.p.m.	0.75 max.	0.75 max.	0.75 max.
Copper, p.p.m.	1.0 max.	1.0 max.	1.0 max.
Aluminum, p.p.m.	3.0 max.	3.0 max.	.....
Total solids, p.p.m.	60.0 max.	40.0 max.	....
Ash, % by wt.	....	....	0.01 max.
APHA[a] color, max.	5	5	....
Appearance	Clear	Clear	Clear (slight turbidity permitted)

[a] American Public Health Association.

The scale tank is loaded with a maximum of 105,000 pounds of solution containing 41% formaldehyde. With a capacity of 12,000 gallons, the tank could hold 110,000 pounds of solution; filling to capacity, however, would make adequate agitation impossible. A side-entering mixer (*23E*) with a 20-inch propeller driven at 420 r.p.m. provides complete mixing during the final adjustment of product concentration. About an hour is required for blending to specification, and an additional half hour is allowed before sampling to determine final concentrations.

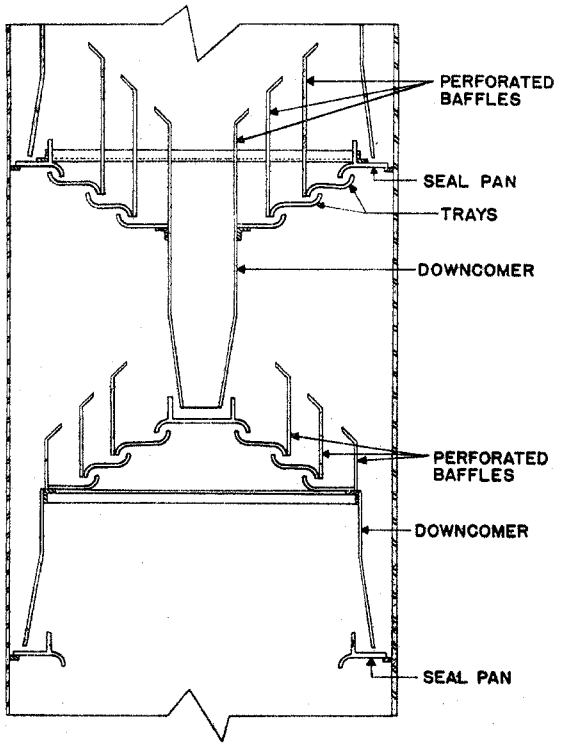


Figure 5. Cascade-Type Trays Used in Final Absorber and in Methanol Stripping Column

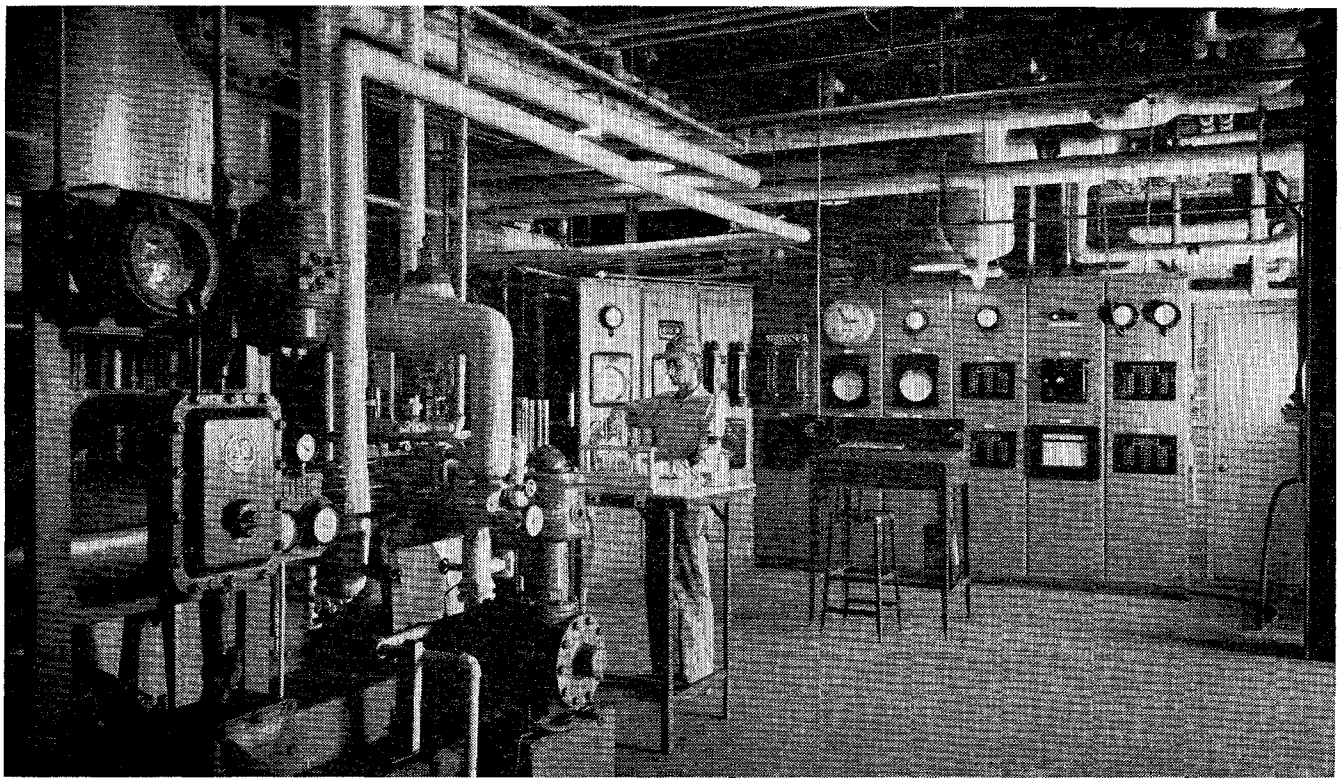
The major portion of Spencer's product is sold as 37% formaldehyde solution, containing less than 1% methanol by weight. For customers desiring an inhibited product, methanol is blended into the 37% solution, normally to a concentration of about 7%. Methanol for this purpose is drawn from the main scale tank and blended into the product solution.

Spencer sells a small amount of 45% formaldehyde, containing less than 1% methanol, but to make this product it is necessary to change the operating conditions for the distillation column. For products containing 41% formaldehyde or less, column operation is held constant, and diluents (primarily methanol and water) are blended in. Table I gives specifications for the three major formulations shipped from the Chicago Works.

Most of Spencer's production is shipped in tank cars or tank trucks. A limited demand for specialty products, such as inhibited 37% solution used by sugar refineries, is satisfied by shipping in 55-gallon drums. This particular specialty is inhibited with 10% methanol in summer and 12% methanol in winter, to prevent polymerization.

Start-Up

A high degree of coordination is required in start-up of the formaldehyde plant in order to eliminate the danger of explosion or other mishaps and to minimize the time and materials consumed in reaching normal operation. Starting "cold" after a prolonged shutdown, it takes approximately 4 hours to bring



Titrating Absorber Bottoms for Formaldehyde Content. Plant Central Control Panel Is Shown in Background

the plant up to capacity. In describing the steps necessary for placing the plant on stream, the operating manual in use at Spencer's Chicago Works places first emphasis on complete safety.

After the process cooling water pumps have been placed in service, water-line valves to and from all coolers and condensers are opened. The recycling of condensate in the final absorber and of formaldehyde-methanol-water solution in the primary absorber is then begun. Next, the recycling of mild caustic solution through the air scrubber is started.

At this point, the methanol evaporator is provided with enough steam to bring it up to 25% of normal methanol vapor output; the vapors produced during this period are allowed to pass unchanged through one of the converter banks to the primary absorber. Air flow is brought up to 25% of the normal operating rate, and the first bank of converters is lighted.

Both air and methanol rates are increased to 50% of normal flow, and the excess gases are allowed to pass through a second bank of converters and into the primary absorber. The second bank of converters is then lighted.

As the liquid level builds up in the bottom of the first absorber, the excess is transferred to the other primary absorber. When both primaries have accumulated the proper amount of solution, any further excess is diverted to the still feed tank. As the formaldehyde concentration builds up to the proper value in the primary absorber, fresh condensate is admitted to the final absorber, while solution is withdrawn from the bottom of the final absorber and fed to the primary. Solution from the primary is withdrawn and transferred to the still feed tank.

With the absorption system thus in operation, air and methanol vapor flows are increased and the two final banks of converters are lighted. The primary absorber for these two banks is cut fully into the absorption system, and the formaldehyde producing and collecting operation of the plant is on stream. As a final step, the methanol stripping still is brought up to operating conditions, and the feed rate is adjusted to coincide with the rate of solution drawoff from the primary absorbers.

Throughout the plant start-up, close attention must be given to the air-methanol ratio in order to prevent the formation of vapor mixtures in the explosive range while maintaining the desired range for the reaction. In addition, reboiler and primary absorber solutions must be analyzed frequently to prevent transferring unsatisfactory product to the product scale tank.

INSTRUMENTATION

The Spencer plant at Chicago is equipped for automatic control wherever possible, and instrumentation plays a very important role in maintaining proper operation of the entire plant. All the significant process variables are continuously controlled and recorded, with a central panel board providing virtually complete information on operation at any given instant.

Recording temperature controllers (*3E*) are used to maintain chosen temperature levels on the process air line and the methanol vapor line. Recording temperature control valves (*11E*) control the flow of steam into the air preheater and methanol superheater in response to demand from the primary temperature controllers. Indicating pressure controllers (*4E*) on the methanol evaporator, methanol vapor line, and process air line, assist in maintaining proper rates of flow. A recording ratio flow controller (*5E*) in conjunction with a recording ratio flow control valve (*12E*) adjusts flow of methanol vapor and process air to maintain a fixed ratio of oxygen to methanol in the converters.

A liquid level controller (*13E*) admits methanol feed to the evaporator to replace the methanol as it evaporates and flows into the process lines. The system of controls on the two principal raw feed lines is completed by indicating pressure control valves (*14E, 15E*) on the process air line, methanol vapor line, and the steam line to the methanol evaporator.

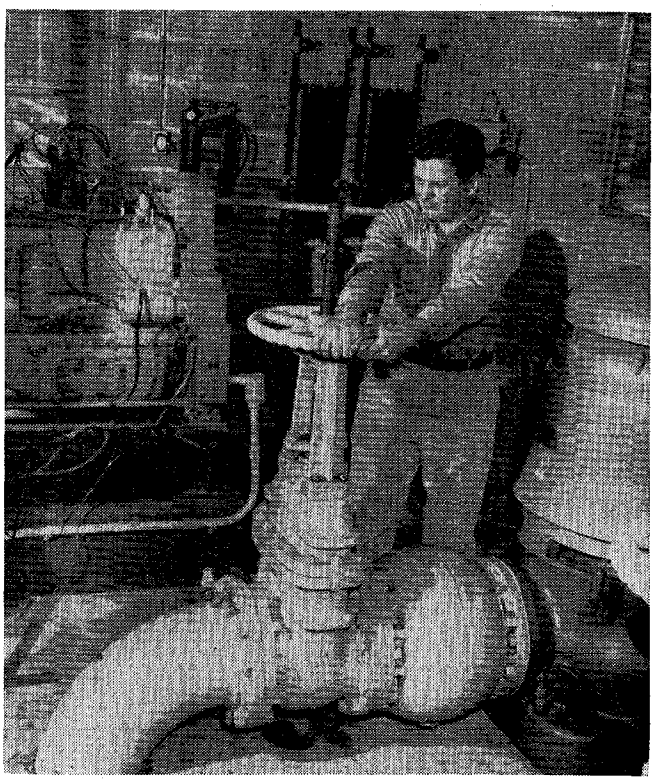
The methanol flow rate for a chosen rate of formaldehyde production is set by a manual control valve (*16E*) on the methanol vapor line, and all other controls function in accordance with the value established for this variable. Indicating manometers (*21E*) measure static pressure in the process air blower discharge

line, and differential pressures over each of the four banks of converters.

Temperatures in the 100 individual converters are measured by means of iron-constantan thermocouples, made of 20-gage thermocouple wire and set into 1/2-inch outside diameter wells. The temperature in any converter can be observed by throwing a switch to connect the given thermocouple with a single-point indicating potentiometer (*22E*).

Another completely integrated system of instruments maintains control over the absorption and purification of the formaldehyde produced. Liquid level controllers (*17E*) regulate the amount of liquid holdup in the primary and final absorbers, the methanol stripping column reflux accumulator tank, and the still reboiler. Each of these controllers actuates a liquid level control valve (*18E*). These in turn regulate the rates of liquid drawoff from the primary and secondary absorbers, the rate of recycle of methanol from the reflux accumulator tank to the evaporator, and the withdrawal of finished product from the reboiler.

Recording flow controllers (*6E*), coupled with recording flow control valves (*19E*), adjust the rate of flow of feed to the stripping still and of reflux to the still head. The ultimate control point for operation of the methanol stripping still is the temperature of the liquid on tray 26. This temperature is maintained constant at a chosen level by means of an indicating temperature controller (*7E*); the latter actuates an indicating temperature control valve (*20E*) which adjusts the flow of steam to the reboiler. Numerous pressure gages, indicating thermometers, pressure relief valves and rupture disks, vacuum relief valves, and flame arresters function as auxiliaries to the more important instruments for process control.



Process Water Intake Situated at River's Edge

ANALYTICAL CONTROL

Constant surveillance is maintained over all incoming raw materials as well as over the properties of the end products shipped from the plant. The most important phase of the raw materials checking program is complete analysis of each tank car of methanol before it is accepted for use. The analysis for a typical sample of acceptable methanol is given in Table II.

In measuring permanganate-reducing substances, a sample of methanol is mixed with a test solution containing 0.2 gram of potassium permanganate per liter. The value recorded is the number of minutes that pass before the mixture develops a color intensity matching that of an arbitrary standard.

Methanol color is considered acceptable if a colorimeter shows it to be lighter than that of an aqueous solution of 3 mg. of potassium dichromate per liter.

Hydrocarbon content is considered sufficiently low if no cloudiness appears on diluting and shaking 1 volume of the methanol with 2 volumes of distilled water.

In testing the intermediate processing streams and the final product formulations, relatively simple analytical procedures are used. Formaldehyde content is determined by the sodium sulfite method, based on the reaction of formaldehyde with sodium sulfite to give free sodium hydroxide and a sulfite-aldehyde addition product. The reaction is specific, rapid, and quantitative

$$HC(=O)-H + Na_2SO_3 + H_2O \longrightarrow NaOH + CH_2(NaSO_3)OH \quad (15)$$

Methanol content of process streams or of product ready for shipment is determined by specific gravity measurements, using a hydrometer. With formaldehyde content previously determined quantitatively, methanol content can be derived from tables of concentration versus specific gravity for formaldehyde-methanol-water solutions.

Acidity, which is due almost entirely to the presence of formic acid, is determined by titration with 0.1 *N* sodium hydroxide solution, to a thymol blue end point. The small quantities of metallic ions present are measured colorimetrically, using potassium thiocyanate for iron, potassium ethyl xanthate for copper, and morin solution for aluminum.

MATERIALS OF CONSTRUCTION

To minimize corrosion problems, Spencer has made extensive use of stainless steel throughout its plant. All lines with which formaldehyde comes into contact are made of stainless steel, usually Type 347. In some of the more critical locations, such as in the working parts of pumps and valves, Type 316 and Type 304 are employed. Other materials that have been found to give good service in contact with formaldehyde are rubber-lined steel, acid-resistant enamel, and stainless-clad steel. Corrosion resistance of stoneware, porcelain, and glass-lined aluminum or steel is satisfactory, but these materials are not always mechanically acceptable for use in formaldehyde processing equipment.

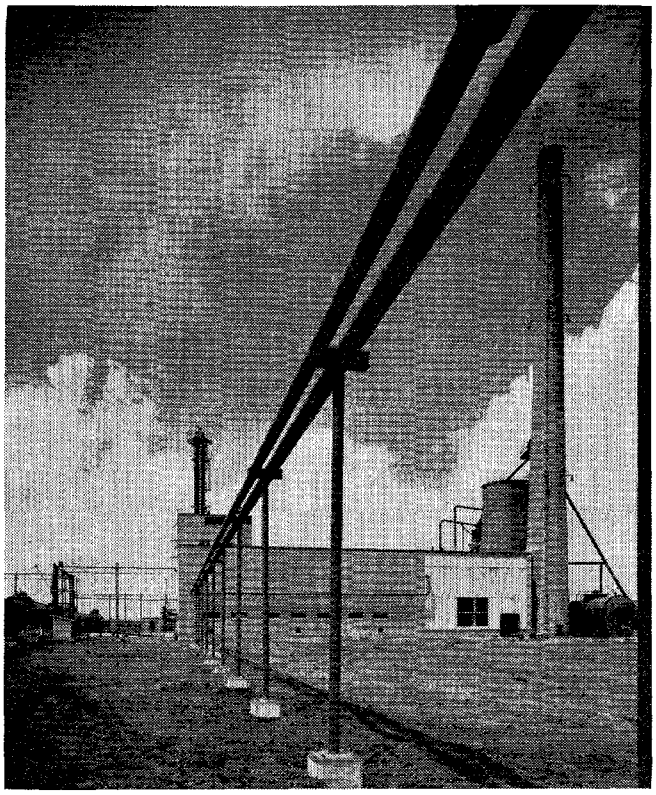
ECONOMICS

The initial investment for construction of the Chicago plant was $1,300,000; Spencer established a 15-year period for amortization. Both construction and equipment costs have risen significantly since the Spencer plant was built, but it is probable that an identical plant could still be erected and equipped with a total investment of less than $2,000,000.

TABLE II. PROPERTIES OF TYPICAL SAMPLE OF METHANOL, ACCEPTABLE FOR FORMALDEHYDE PRODUCTION

Methanol content, wt. %	99.91
Distillation range	64.3–64.9° C.
Nonvolatile matter	0.0006 g./100 ml.
Acidity (as acetic acid), wt. %	0.003
Aldehyde and acetone content, wt. %	0.001
Permanganate-reducing substances	30 minutes min.[a]
Color	Acceptable[a]
Hydrocarbons	Acceptable[a]

[a] See text for explanation.



A Portion of Spencer's Formaldehyde Output Flows through Overhead Pipeline to Neighboring Resin Plant of Catalin Corp.

Over-all plant efficiency for the Chicago Works averages well over 80%. Since this figure is based on the weight of methanol as loaded into tank cars at the Pittsburg plant and the weight of formaldehyde loaded out at Calumet City, it must take into account any and all small losses along the way.

When operating at its normal output of 50 tons per day, the plant consumes 2.25 pounds of steam per pound of formaldehyde produced and uses 2,500,000 gallons of water per day for all purposes. Steam is currently produced by coal-fired boilers. Savings of up to $10,000 per year are expected with a switch to natural gas as fuel; this change is in the immediate offing, with gas mains already partially installed. Gas was requested 4 years ago at the time of Spencer's initial decision to build, but gas supplies in the Chicago area were inadequate until the recent completion of a new 30-inch line from Texas.

FUTURE PROSPECTS

The optimistic market outlook which existed when Spencer entered the field proved to be justified, and total formaldehyde production has climbed nearly 60% during the intervening 3 years. The climb is still in progress, although there is some disagreement as to whether the rate of climb will remain very high.

On the bullish side, the Defense Production Authority (DPA) has recently set a goal of 1.675 billion pounds per year as a minimum for formaldehyde production capacity in the United States by January 1955. This goal represents an increase of more than 25% over the capacity that existed on January 1, 1951, DPA's usual reference date.

On the bearish side, a few tehnical men closely connected with markets feel that the growth curve will level off very soon—assuming no large scale new developments are in immediate prospect. From a condition of moderate to severe shortage 3 years ago, the industry has increased its output until today supplies are very nearly in balance with demand. Some observers feel that there may even be some excess production for a time, until expanding markets can again overtake production.

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Processing Equipment

(1E) Alpha Tank & Sheet Metal Mfg. Co., St. Louis, Mo., methanol-air mixer.
(2E) Elliott Co., Chicago, Ill., steam turbines, Model 2-AY.
(3E) Foxboro Co., Foxboro, Mass., recording temperature controllers, Model 40, pneumatically operated.
(4E) *Ibid.*, indicating pressure controllers, Model 40, pneumatically operated.
(5E) *Ibid.*, recording ratio flow controller, Model 42, pneumatically operated.
(6E) *Ibid.*, recording flow controllers, pneumatically operated.
(7E) *Ibid.*, Dynalog Stabilog indicating temperature controller.
(8E) Griscom-Russell Co., Kansas City, Mo., primary product cooler with twin G-Fin sections.
(9E) Koch Engineering Co., Wichita, Kan., Kascade trays for final absorber and methanol stripping still.
(10E) Lamson Corp., Syracuse, N. Y., centrifugal blowers, 1000 cu. ft./min. at 3500 r.p.m.
(11E) Mason-Neilan Regulator Co., Boston, Mass., 3/4-inch diaphragm control valves, No. 38, air-opening.
(12E) *Ibid.*, 6-inch diaphragm ratio flow control valve, No. 38, air-opening.
(13E) *Ibid.*, 3/4-inch diaphragm liquid level control valve, No. 38, air-opening.
(14E) *Ibid.*, 2-inch diaphragm indicating pressure control valves, No. 38, air-opening.
(15E) *Ibid.*, 6-inch diaphragm indicating pressure control valve, No. 38, air-opening.
(16E) *Ibid.*, 2-inch diaphragm manual control valve, No. 38, air-opening.
(17E) *Ibid.*, liquid level controllers, No. 12600, displacement type.
(18E) *Ibid.*, 3/4-inch diaphragm liquid level control valve, No. 38, air-opening.
(19E) *Ibid.*, 1-inch and 1 1/2-inch diaphragm recording flow control valves, No. 38, air-opening.
(20E) *Ibid.*, 4-inch diaphragm indicating temperature control valve, No. 38, air-opening.
(21E) Meriam Instrument Co., Cleveland, O., indicating manometers, U-type, water or mercury fluid.
(22E) Minneapolis-Honeywell Regulator Co., Brown Instruments Div., Philadelphia, Pa., single-point indicating potentiometer.
(23E) Mixing Equipment Co., Rochester, N. Y., Lightnin gear-drive mixer, 7 1/2-hp. motor.
(24E) Nooter, John, Boiler Works, St. Louis, Mo., Type 304 stainless steel evaporator.
(25E) Ross Heater & Mfg. Co., Kansas City, Mo., horizontal tube, kettle type reboiler.
(26E) Trane Co., Kansas City, Mo., finned heating coils for methanol vapor superheater and air preheater.

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